

The Polymer Incorporated Method for the Preparation of Highly Active Heterogeneous Palladium Catalysts

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Palladium catalysts are often used in organic synthesis, and versatile transformations using palladium catalysts have been developed.¹ While homogeneous palladium catalysts are used in many cases, heterogeneous palladium catalysts are crucial for their application to industry because they are easily recovered and reused. However, few successful examples of heterogeneous palladium catalysts have been reported. While immobilization of palladium catalysts onto inorganic supports is possible, leaching of the catalysts during and/or after reactions is a serious problem.² On the other hand, polymer-supported phosphine and amine ligands have been developed to immobilize palladium catalysts onto polymers.³ In this case, however, reactivity of the immobilized palladium catalysts is often lower than that of the corresponding original catalysts. To address these issues, we have investigated a new method for immobilizing palladium catalysts onto polymers. In this report, we describe "the polymer incorporated (PI) method",⁴ which can create recoverable, reusable, and highly active heterogeneous palladium catalysts for hydrogenation, carbon–carbon, and carbon–oxygen bond-forming reactions.

In the PI method, a catalyst is first microencapsulated.^{5,6} That is, a polymer is dissolved in an appropriate solvent, and a catalyst is added to this polymer. After being cooled, microcapsules formed are washed and dried to afford a microcapsulated catalyst. It has already been shown that the catalyst locates not only inside the capsules but also on the surface or close to the surface of the capsules. The microcapsules formed are then cross-linked to afford the desired catalyst.

On the basis of this idea, we designed epoxide-containing copolymers (1a–c), which were prepared by radical polymerization of styrene, 4-vinylbenzyl glycidyl ether, and methacrylic acid or alcohol (2 or 3) (Figure 1). Copolymer (1a–c) was dissolved in THF at room temperature, and to this solution was added Pd(PPh₃)₄ as a core. After hexane was added, cosolvents were found to envelop the core dispersed in the medium. The mixture was left to stand at room temperature to form microcapsules containing Pd. After filtration, wash, and dry, the catalyst capsules were then stirred at 120 °C for 2 h to afford polymer incorporated palladium (PI Pd).^{5,7} During this preparation, 4 equiv of PPh₃ was recovered from the washings, and no PPh₃ was observed in PI Pd measured by ³¹P SR-MAS NMR⁸ and X-ray photoelectron spectroscopy (XPS) analyses. From these results, it was assumed that phosphine-free Pd(0) was formed by using the PI method.⁹ It should be noted that normally unstable ligand-free Pd(0) was readily prepared and could be stored at room temperature in air.

PI Pd (4a–c) thus prepared were first used in hydrogenation. While several homogeneous catalysts have been used in reduction reactions, heterogeneous catalysts have often been employed in many synthetic stages in laboratories as well as industry.¹⁰ Although Pd/C is one of the most popular heterogeneous catalysts, leaching of Pd and ignition are known to be serious problems especially when reduction is performed in large-scale experiments. We first

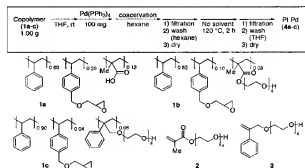
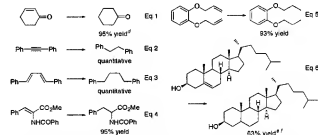


Figure 1. Preparation of polymer incorporated (PI) Pd (4a–c) from copolymers (1a–c).

Table 1. Hydrogenation of Benzalacetone and Other Examples^a


















Pd	yield (%) ^b				
	first	second	third	fourth	fifth
PI Pd 4a ^b	81				
PI Pd 4b ^b	93	80	88	82	87
PI Pd 4c ^b	85	80	87	91	90
5% Pd/C	91				
Pd(PPh ₃) ₄	0				



^aUnless otherwise noted, the hydrogenation of olefin (0.5 mmol) was carried out in the presence of PI Pd (5 mol %) in THF (5 mL) and an atmosphere of hydrogen (1 atm) for 1 h. Catalysts 4b and 4c were recovered and reused after simple filtration and drying. ^bNo peaks of palladium metal were observed in fluorescence X-ray analysis. ^c5/6 = 95/5. ^dDetermined by gas chromatography. ^eReaction was carried out in dichloromethane (5 mL.) for 24 h. ^fDetermined by ¹H NMR.

tested PI Pd in the hydrogenation of benzalacetone, and the results are shown in Table 1. Among PI Pd tested, 4c gave the best result (entries 1–3).¹¹ The reduction was completed within 1 h in THF under ordinary pressure, and it should be noted that the catalyst was recovered quantitatively by simple filtration and that the same levels of yields were obtained even after the fifth use. Moreover, it was confirmed by fluorescence X-ray analysis that no leaching of Pd from the catalyst occurred. We surveyed reduction of other substrates using PI Pd, and in all cases the reactions proceeded

Table 2. Allylation Reactions Using PI Pd 4c^a

Allylic carbonate	Nucleophile	Product	Yield (%)
			88
			94
			51
7			94
7			quant
7			96
7			quant

^a All reactions were carried out using PI Pd 4c (5 mol %) and PPh₃ (5 mol %) in THF under reflux for 2 h.

smoothly to afford the desired products in high yields (eqs 1–6). The activity of PI Pd was comparable to that of 5% Pd/C (entry 4), but no ignition occurred using PI Pd. It is also noteworthy that PI Pd was much more active than the original catalyst, Pd(PPh₃)₄. The reaction did not proceed at all using Pd(PPh₃)₄ under the same reaction conditions (entry 5). Furthermore, it was revealed that the reduction also proceeded smoothly using <0.1 mol % of PI Pd.

PI Pd (4a–c) were then applied to allylic substitution reactions, one of the representative carbon–carbon bond-forming reactions.¹² We chose the reaction of allyl methyl carbonate (7) with dimethyl phenylmalonate (8) as a model, and several reaction conditions were examined.¹³ It was found that the allylation reaction proceeded in the presence of PI Pd (5 mol %) and PPh₃ (5 mol %) in THF under reflux conditions. While 4a gave lower yields, the activity of 4b and 4c was high, and the desired allylation adducts were obtained in excellent yields. The catalysts were recovered by simple filtration and reused several times. In the case of 4b, however, leaching of palladium from 4b occurred in the fourth and the fifth use. On the other hand, no leaching of palladium was observed in the reactions using 4c even after the fifth use, and the reactions proceeded smoothly to afford the desired adducts in high yields in all cases.

Several examples of allylic substitution reactions using the PI Pd 4c are summarized in Table 2. Malonate and β -ketoester smoothly reacted under these conditions to afford the corresponding allylation products in high yields. Moreover, PI Pd 4c was successfully applied to carbon–oxygen bond-forming reactions. That is, phenol or naphthol derivatives smoothly reacted with 7 to afford the corresponding allyl phenyl or allyl naphthyl ethers in high yields. It should be noted that 4-nitrophenol also worked well to produce allyl 4-nitrophenyl ether quantitatively. It was already reported that the reactivity of phenol or naphthol derivatives having electron-withdrawing groups such as a nitro group decreased significantly even using very reactive homogeneous palladium systems.¹⁴ In this reaction, it was exciting to demonstrate that PI Pd 4c was more reactive than the homogeneous Pd catalysts.

Thus, we have developed an efficient method for immobilizing a palladium catalyst onto polymer. The method named “the polymer incarcerated (PI) method” is novel, and the following characteristic features are noted. (i) The method is operationally simple, and the desired immobilized catalyst is readily prepared. (ii) By using the

PI method, a normally labile species such as ligand-free Pd(0) is stabilized and can be stored at room temperature. (iii) PI Pd is successfully used in reduction, carbon–carbon bond-forming reactions, and carbon–oxygen bond-forming reactions. (iv) The catalyst is recovered quantitatively by simple filtration and reused several times without loss of activity, and no leaching of Pd is observed. (v) The higher activity of PI Pd as compared to even homogeneous Pd catalysts has been demonstrated. (vi) Ignition has never occurred in all of the PI Pd-catalyzed reactions we tested. PI Pd is regarded as a safe catalyst. (vii) The PI method has been shown to be effective in immobilizing Pd(0) species onto polymers, and this method is expected to be useful to immobilize other metal species onto polymers directly. Further studies to develop other PI catalysts are now in progress.

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Supporting Information Available: A table of details in the reaction of 7 with 8 and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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